Supported gold clusters and cluster-based nanomaterials: characterization, stability and growth studies by *in situ* GISAXS under vacuum conditions and in the presence of hydrogen

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This contribution is devoted to study of the thermal stability and growth of gold nanoparticles supported on $SiO_2/Si(111)$ and $Al_2O_3/SiO_2/Si(111)$ as a function of initial cluster size, support material and level of surface coverage. Experimental evidence for "flipping" of two dimensional cluster structures from vertical orientation to horizontal on the support is presented.

KEY WORDS: laser vaporization; gold clusters; cluster structure; molecular beam; size selection; soft-landing; supported clusters; surface coverage; sintering; thermal stability; heat treatment; agglomeration; oxide support; alumina; silica; SiO_2; Al_2O_3; support effect; grazing incidence small angle X-ray scattering; 2-dimensional growth; 3-dimensional growth; hydrogen atmosphere; aggregation; ALD film; GISAXS; isomerization.

1. Introduction

Small nanoparticles possess unique, strongly size-dependent chemical and physical properties that make these particles ideal candidates for a number of applications, including catalysts or sensors due to their significantly higher activity and selectivity than their more bulk-like analogs [1]. In the smallest size regime, nano-cluster catalytic activity changes by orders of magnitude with the addition or removal of a single atom, thus allowing a tuning of the properties of these particles atom by atom [2]. Equally effective tuning knobs are the composition and morphology of the support, which can dramatically change the electronic structure of these particles, leading to drastic changes in both activity and specificity. However, while small gold nanoparticles currently are suggested as the catalyst of choice for selective CO oxidation of H_2 streams within the hydrogen initiative, the Achilles heal of these particles remains their increased mobility at elevated temperatures or when exposed to mixtures of reactive gases. The mobility of the particles may cause their aggregation leading to the alteration of their size-specific physical and chemical properties [3]. In the presented paper, the issue of thermal stability and growth of atomic gold clusters and nanoparticles produced by cluster deposition on oxide surfaces is addressed by employing synchrotron X-ray radiation as a function of deposited cluster size, level of surface coverage, temperature and time of heat treatment under vacuum conditions and in the presence of hydrogen. The temperature region of aggregation was determined by gradually heating up the samples and recording two-dimensional *in situ* X-ray scattering images during the heat treatment. The real-time kinetics of cluster aggregation at a constant temperature was then monitored by acquiring X-ray data for several hours.

2. Experimental

2.1. Support materials

As support materials, naturally oxidized silicon wafers ($SiO_2/Si(111)$) and thin alumina films prepared by atomic layer deposition (ALD) technique ($Al_2O_3/SiO_2/Si(111)$) were used. These surfaces are easily prepared by ALD using a two-step procedure (AB) for producing a single oxide monolayer. ALD is a thin film growth method utilizing a pair of self-limiting chemical reactions between gaseous precursor molecules (A and B) and a solid surface to deposit films in a monolayer-by-monolayer fashion [4]. Exposing the initial surface to reactant A results in the self-terminating adsorption of a monolayer of A species. The resulting surface becomes the starting substrate for reaction B. Subsequent exposure to molecule B will cover the surface with a

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monolayer of B species. Consequently, one AB cycle deposits one monolayer of the compound AB and regenerates the initial substrate. The $SiO_2/Si(111)$ substrates were coated by Al_2O_3 ALD using alternating exposures to trimethyl aluminum (TMA, Aldrich) and deionized water in a viscous flow ALD reactor at a temperature of 200 °C [5]. Ultrahigh purity N_2 carrier gas was used at a mass flow rate of 360 sccm and a pressure of 1 Torr. The reactant exposure times were 1 s and the purge times between exposures were 5 s. These conditions yield an Al_2O_3 ALD growth rate of 1.2 Å/cycle [6].

2.2. Cluster deposition

The continuous beam of gold clusters is generated in a recently developed high-flux laser vaporization cluster source which utilizes the frequency doubled output of a Quantronix 532DP-MM Nd:YAG laser operating at 4.5 kHz (see figure 1). The cluster beam passes through a biased skimmer into the second differentially pumped vacuum stage and then into the third stage where the mass spectroscopic analysis of the produced clusters takes place prior to deposition. The charged clusters are deflected into an ion-optics setup with an incorporated mass spectrometer for the pre-selection of narrow cluster distributions in the size range Au_n^+, $n = 2,...,10$, with 2–5 dominant sizes. The flux of clusters soft-landing on the surface is monitored in real-time using a Keithley Model 6487 picoammeter equipped with an internal voltage source. The kinetic energy of clusters landing on the surface is controlled by biasing the substrate. Typical deposition energy is ~1 eV/atom or less. Surface coverages up to 45% of atomic monolayer equivalents (ML) were employed, yielding covered areas with a typical diameter of 3–5 mm.

2.3. Grazing incidence small angle X-ray scattering (GISAXS)

The X-ray scattering experiments were performed at the BESSRC 12-ID beam-line of the Advance Photon Source of the Argonne National Laboratory. This setup allows acquisition of 2-dimensional scattering patterns during heat treatment of the sample, as a function of temperature and time. The subsequent analysis of the data gives information about the average size and shape of supported nanoparticles, as well as on the distribution of cluster size and anisotropy of the particle shape. In order to improve the signal to noise ratio, anomalous GISAXS (AGISAXS) was used for samples with very low coverages [7, 8].

3. Results and discussion

3.1. Formation of larger aggregation from deposited clusters at higher levels of surface coverage

The size of the nanoparticles formed on the surface upon cluster deposition and their thermal stability exhibited a very strong dependence on the initial size of the clusters, level of surface coverage and material of the support. When applying surface coverages higher than 5% atomic monolayer equivalent (ML), considerable aggregation of the clusters into nanometer-size particles with narrow size distribution prevailed. As an example, the deposition of a cluster distribution centered around the dominant Au_4 at 25% ML coverage on silica yielded two particle sizes with radii of gyration $R_{g1} = 3.1$ Å and $R_{g2} = 12.6$ Å with number ratio $N_1/N_2 = 0.56$. (The correlation between the radius of gyration R_g obtained from data analysis and the diameter of the particles d is defined as $d = 2 \times 1.29 \times R_g$). Both R_g
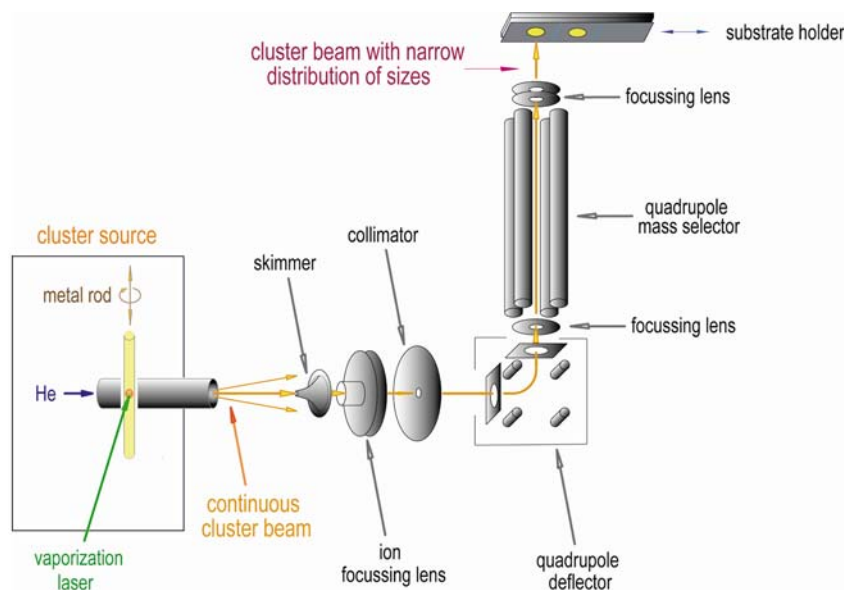

Figure 1. Scheme of the cluster deposition setup.

values correspond to aggregates formed from deposited clusters. When depositing Au_{6-10} clusters at 5% ML on 1 nm thick alumina film, aggregate formation prevailed yielding particles with average radii of gyration of 4.6 and 12.7 Å and $N_1/N_2 = 0.69$. In the case of deposition of dominantly Au_3 and Au_4 clusters on 1 ML Al_2O_3/SiO_2/Si(111) at 15% ML, two particle sizes with $R_{g1} = 1.8$ Å and $R_{g2} = 12.6$ Å with number ratio $N_1/N_2 = 0.82$ were observed, with R_{g1} matching the size of the gas-phase gold trimer and tetramer. The heat treatment of the sample indicated a complex multi-step agglomeration process [8]. With decreasing surface coverage, the fraction of non-aggregated clusters significantly increased. The heat treatment led to final particle sizes determined by initial cluster size, coverage and length of treatment. Striking results were observed when depositing 2.5% ML of Au_7–Au_{10} clusters on SiO_2/Si(111): particles of one size with $R_g = 3.1$ Å, corresponding to Au_{20} were formed, indicative of a formation of "dimers" and "trimers" from initially deposited hexa- to decamers. Moreover, these particles exhibited extraordinary and unexpected thermal stability as well, not undergoing aggregation until 400 °C (figure 2(a)), when an onset of a slow agglomeration takes place (figure 2(b)). The final particle size leveled off at ~1.2 nm diameter and provided additional proof of the feasibility of controlling the size of assembled particles by varying the size of deposited clusters, level of

surface coverage, temperature and duration of the heat treatment [7, 8].

3.2. Effect of substrate material and level of coverage on the size of supported fabricated at room temperature

Au_{6-10} clusters were deposited on silica and 1 ML alumina film at coverages between 2 and 6% ML (figure 3). The comparison of the obtained distributions shows that in the case of the silica surface, a considerable aggregation into larger particles, accompanied by broadening of the distribution, takes place at 4.2% ML (figure 3(a)). On the contrary, the alumina surface posses a high potential for preventing agglomeration of the deposited clusters (figure 3(b)). This observation is of central importance for the preservation of the initial cluster size and for the study of the properties of these isolated particles.
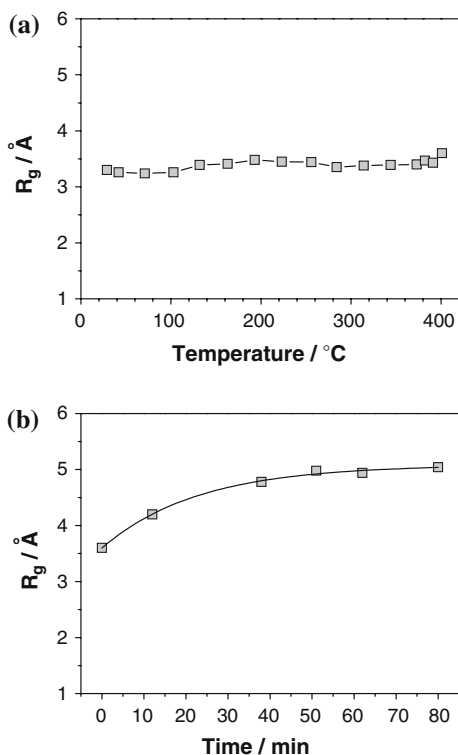

Figure 2. Mean radius of gyration R_g ($R = 1.26 \times R_g$) of the gold particles formed from Au_{7-10} clusters on SiO_2/Si(111): (a) R_g as a function of temperature during heat treatment of the sample; (b) real-time kinetics of aggregation at 400 °C.

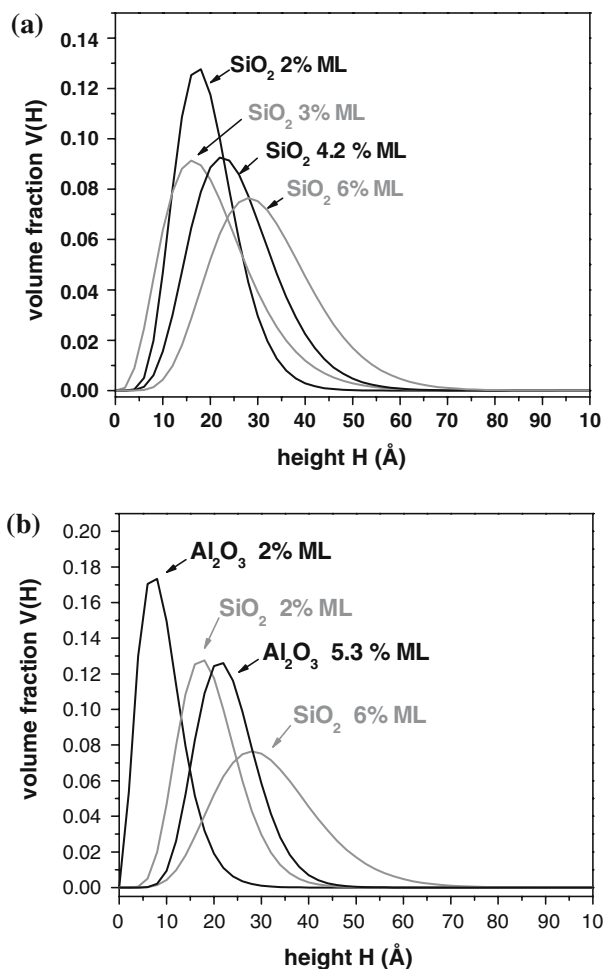Figure 3. (a) Height distribution of supported clusters on SiO_2/Si(111) as a function of the level of surface coverage with Au_{7-10} clusters in atomic monolayer equivalents. (b) Height distribution of supported clusters on SiO_2/Si(111) and 1 ML Al_2O_3 film on SiO_2/Si(111) as a function of the level of surface coverage with Au_{7-10} clusters in atomic monolayer equivalents.

3.3. Thermal stability and kinetics of aggregation of supported clusters in vacuum and in the presence of hydrogen

A pair of identical samples was prepared by depositing Au_{4-10} clusters on $SiO_2/Si(111)$ support at 2% ML coverage. This low level of coverage was chosen in order to prevent the agglomeration of clusters after landing on the surface. Both samples were heated using the same temperature ramp: during the first 4 h the temperature was monotonically increased from room temperature to 400 °C, then during the second 4 h period, the temperature was kept constant at 400 °C and anomalous scattering data were recorded in regular intervals (see insert in figure 4(b)). In the case of the sample heated in the absence of hydrogen the increase in temperature did not induce any noticeable change in particle width in the temperature range up to 400 °C. After another 2 h were elapsed, a slow increase in the lateral dimension was observed. The height of the particles remained practically unchanged during the 8 h heat treatment, thus
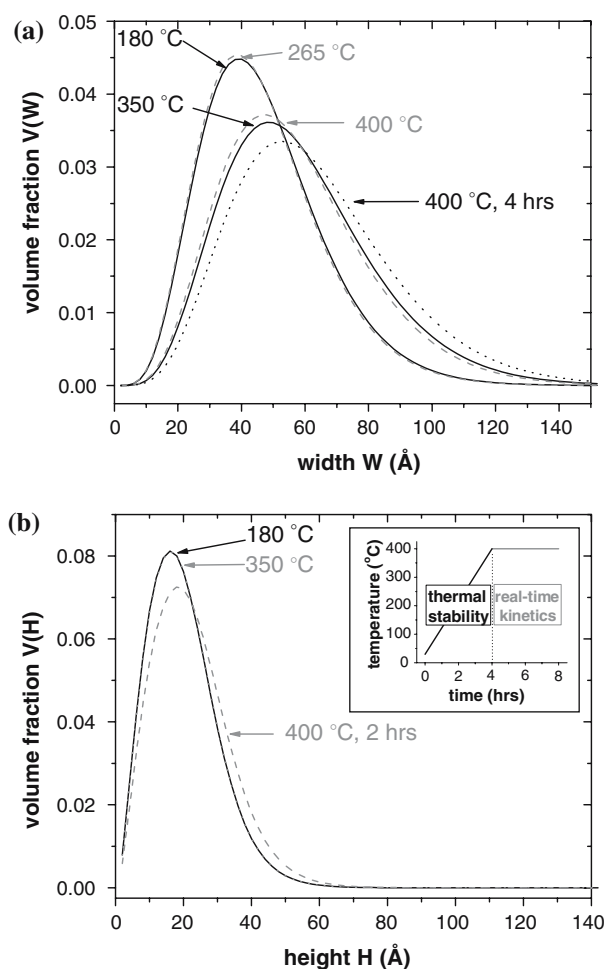
indicating a two-dimensional nanoparticle growth. Figure 5 shows the results of the heat treatment of the gold clusters in the presence of hydrogen (p_{H2} = 30 mTorr). In contrast to the vacuum treatment, a clear three-dimensional growth with an onset at around 350 °C is observed. Similar 2-D versus 3-D growth was observed in the case of silica supported Pd clusters in the absence and presence of hydrogen, respectively [H.-J. Freund, private communication]. The observation of the 3-dimensional growth of Au nanoparticles may reflect (1) the exothermic process of burning of hydrogen on (some) of the nanoparticles activated on the silica support, (2) reaction of gold particles with hydrogen, and (3) modification of the properties of the cluster/support interface resulting in an increased mobility of the clusters and their subsequent aggregation. The planned X-ray absorption and catalytic reactor studies will provide detailed information about the processes involved.
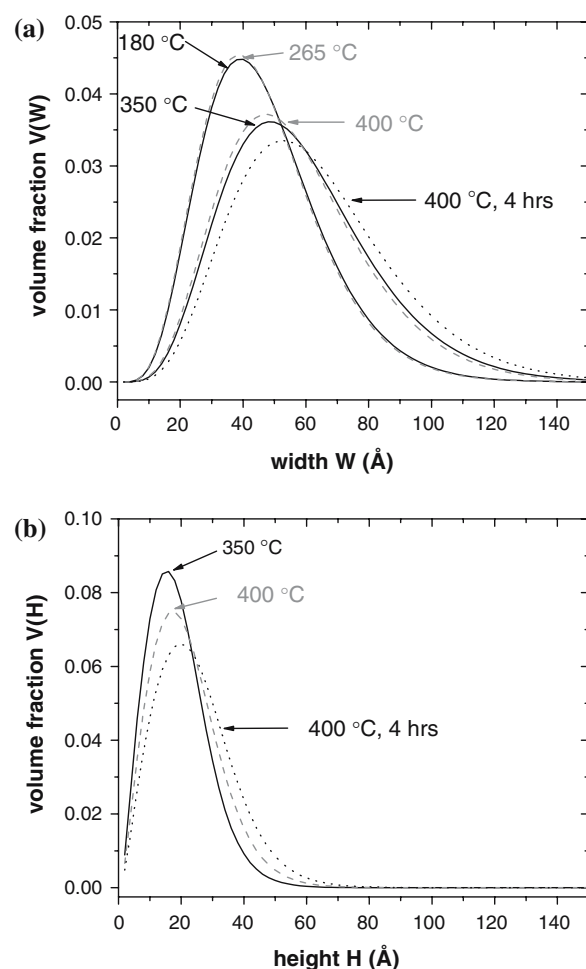

Figure 4. Evolution of the width (a) and height (b) distribution of supported Au_{7-10} clusters on $SiO_2/Si(111)$ during the course of the heat treatment in the absence of H_2. The insert in (b) shows the time profile of the temperature ramp applied.

Figure 5. Evolution of the width (a) and height (b) distribution of supported Au_{4-10} clusters on $SiO_2/Si(111)$ during the course of the heat treatment in the presence of H_2. Identical temperature ramp as shown in the insert of figure 5b was applied.

3.4. Structural transformation of clusters in the lower temperature region

It is a widely accepted view that small supported nanoparticles possess high structural fluxionality and can readily undergo structural transformations during a catalytic reaction. In the course of our systematic studies of the thermal stability of supported gold clusters, we have observed a decrease in the cluster height at the beginning of the heat treatment. Using AGISAXS, it was possible to rule out any alteration in the surface structure which could cause such changes in the observed dimensions of the supported particles. Figure 6 shows the evolution of the Au particle height with temperature before the onset of 3-D aggregation takes place at 350 °C (figure 5). Figure 6(a) shows no change in particle height in the low temperature region (only data at two temperatures are shown for clarity). At 140 °C, the sudden drop in height is accompanied by a sharp narrowing in the width of the distribution as well, indicative of a transition from tall particles to flat lateral structures. Further increase in temperature to ~180 °C yields higher 3-D structures. It is surprising to see that the final particle height produced by the lengthy heat treatment does not exceed the initial particle height. This observation can be explained by changes in deposited cluster structures during heat treatment as described below. Computational and experimental studies performed on gas phase gold clusters show that, depending on the charge, these clusters can accommodate flat equilibrium structures up to Au_8 or higher [9–11].

Very recently, Molina and Hammer have reported very stable planar vertical shapes for small (Au_2–Au_7) clusters supported on MgO [12].

The relativistic effects that cause the 2D structures to be preferred in the gas phase also cause that, upon binding to the oxide, the most active cluster binding sites are the ones along the rim of the 2D cluster, causing such upright configurations to be relatively stable.

Our experimental results provide the first evidence of "flipping" of such two-dimensional cluster structures from vertical into horizontal orientations (which, in the case of MgO, have comparable stabilities [L. Molina and B. Hammer, private communication]); further diffusion and aggregation of horizontal clusters results in an increase of height.

4. Summary and outlook

The presented results clearly demonstrate the powerful combination of the atomic layer deposition, cluster deposition and synchrotron techniques in the synthesis and detailed characterization of exceptionally stable
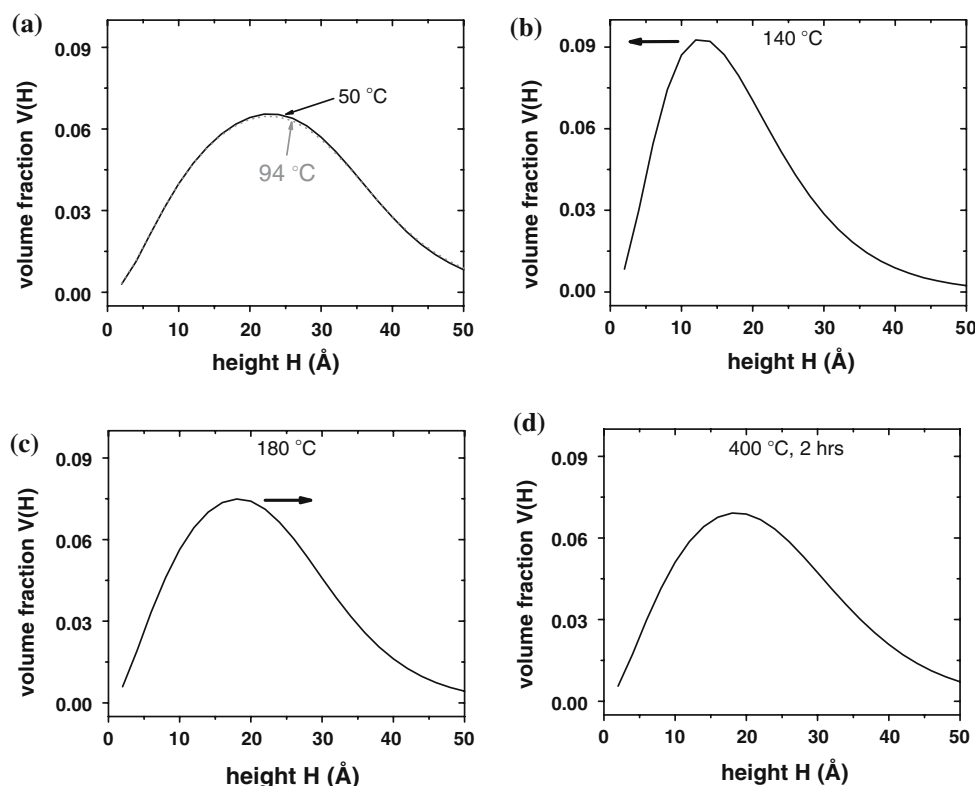

Figure 6. Height distribution of supported Au_{4-10} clusters on SiO_2/Si(111) during the course of the heat treatment in the presence of H_2: the lower temperature range. (a) Height distribution at 50 and 94 °C; (b) shift of the size distribution to smaller values at 140 °C; (c) increase in height at 180 °C; and (d) the final height distribution after 8 h of heat treatment.

model catalyst systems. Such catalysts may find broad applications, for example in hydrogen economy in the design of affordable optimized catalysts for highly selective low-temperature oxidation of CO in the presence of hydrogen—a central issue for removing traces of CO in on-board fuel cell applications. Our results indicate that the final size of supported nanoparticles can be tuned by controlling the initial size of clusters, level of surface coverage and material of the support. Additional control knobs are the temperature and length of heat treatment, as well as the composition and morphology of the support. The techniques used allow for synthesis of highly monodispersed particles designed with atomic precision for molecular level studies of catalysts.

Acknowledgments

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Erratum Figure 4.

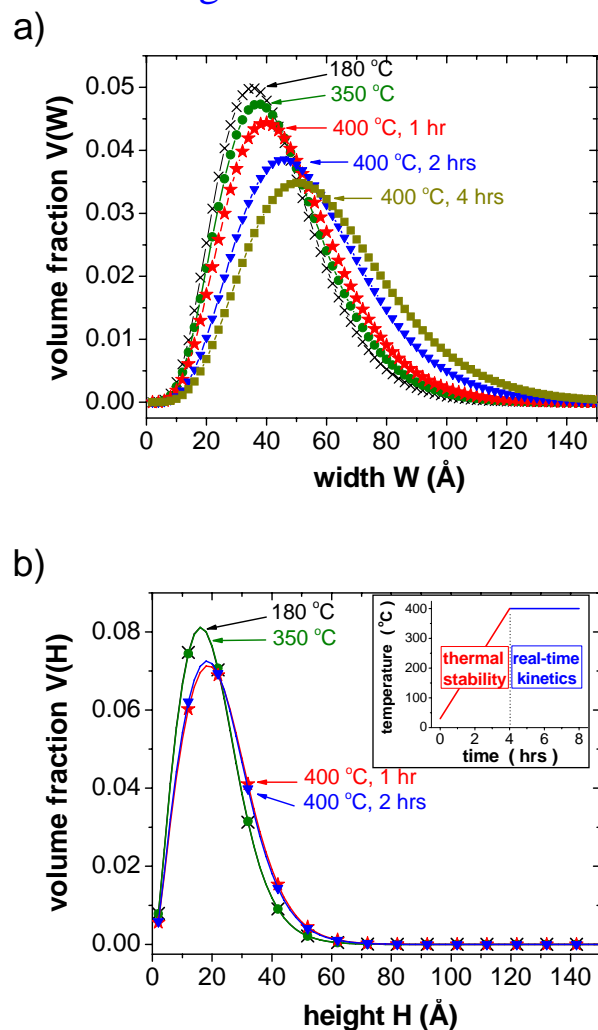**Figure 4.** Evolution of the width (a) and height (b) distribution of supported Au_{7-10} clusters on $SiO_2/Si(111)$ during the course of the heat treatment in the absence of H_2. The insert in (b) shows the time profile of the temperature ramp applied.
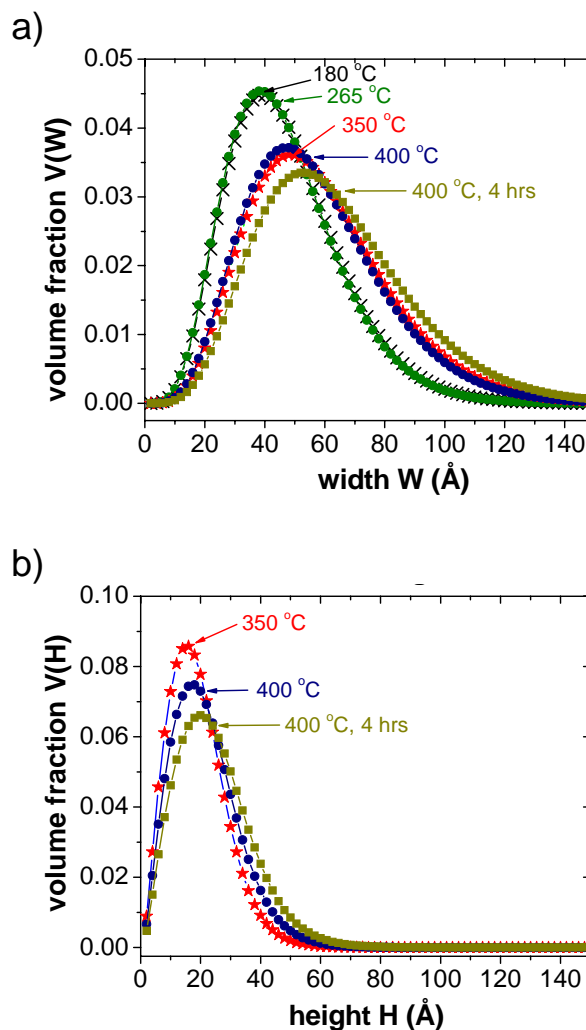
Figure 5. Evolution of the width (a) and height (b) distribution of supported Au_{4-10} clusters on $SiO_2/Si(111)$ during the course of the heat treatment in the presence of H_2. Identical temperature ramp as shown in the insert of Fig. 5b was applied.